

Ocean Storage of CO₂: Experimental Observations of Clathrate Hydrates in Seawater

Robert P. Warzinski (warzinsk@fetc.doe.gov; 412/892-5863)
Federal Energy Technology Center

Gerald D. Holder (holder@engrng.pitt.edu, 412/624-9809)
University of Pittsburgh, School of Engineering, Pittsburgh, PA 15261

Introduction

The deep ocean (>500 m depth) is being investigated for long-term sequestration of CO₂ [1]. At these depths crystalline CO₂ clathrate hydrate (CO₂ · nH₂O, 6<n<8) can form. Theoretically, the hydrate particles should sink in the ocean. This would facilitate sequestration by transporting the CO₂ to even greater depths than used for injection. However, our prior work with CO₂ and freshwater has shown that hydrates which initially form from a two-phase system (freshwater and either gaseous or liquid CO₂) float in the freshwater phase, likely due to CO₂ trapped within the hydrate particles[2]. If floating hydrates form upon injection of CO₂ into the ocean, sequestration would be adversely impacted because the CO₂ would ultimately end up at shallower depths than planned. The hydrate can also form as a shell on buoyant CO₂ drops. This would limit the dissolution of the CO₂ and frustrate the sequestration attempt as the hydrate-encased CO₂ drops rise to unacceptable depths. Formation of the more desirable sinking hydrate was observed when the CO₂ was dissolved in the freshwater prior to reaching hydrate-forming conditions [2].

This paper describes current research on hydrate formation in seawater. Both the relative density of hydrate particles and the impact of a hydrate shell on the dissolution of liquid CO₂ drops were investigated in seawater. Observations of the relative thickness of the hydrate shells are also presented and compared to predictions from a model that was developed to predict the initial and steady-state thickness of these shells.

Approach

Experimental observations were made in a high-pressure, variable-volume viewcell (HVVC) of 10 to 40 cm³ capacity. The HVVC was enclosed in a chamber where the temperature could be maintained in the region of interest (0°C to 10°C). Agitation in the HVVC was provided by a glass-encased magnetic stirring bar. More complete descriptions of the HVVC and the basic procedures have been published [2, 3]. General Purpose Seawater (GPS), salinity around 35, was obtained from Ocean Scientific International, Ltd., Petersfield, Hampshire, U. K. SFC purity (99.99+%) CO₂ was used.

Results

Relative hydrate density

The relative density of hydrate particles at the time of their formation is profoundly affected by the

mode of CO₂ injection. Hydrates formed readily from a single-phase solution of 59.9 mg CO₂ dissolved per gram GPS with agitation at 4°C to 5°C, 150 bar, conditions similar to those anticipated for ocean injection. The initially formed hydrate was icelike in appearance (transparent) and rapidly sank. When a CO₂ drop was subsequently injected in this experiment, the drop rapidly formed a hydrate shell. In contrast to hydrates formed from solution, when the hydrate-covered drop was broken apart with agitation, the hydrate fragments floated in the seawater phase that was at 2.8°C, 151 bar. The fragments were found to sink at higher pressure (approximately 305 bar). The increase to this higher pressure would compress any trapped liquid CO₂ to a density equal to or greater than that of the seawater phase, thus indicating that the cause of the initial buoyancy of the fragments was due to trapped CO₂.

Hydrate formation was not observed from a single-phase solution of 44 mg CO₂ per gram GPS at conditions approximating those anticipated for ocean injection. Sinking hydrate particles did form at more severe conditions, 2°C and at pressures approaching 270 bar. Further work is in progress to better define conditions at which hydrate will form from CO₂ dissolved in seawater.

Effect of hydrate shell on CO₂ drops

Both theoretical and experimental work have been performed to determine the impact of a hydrate shell on the fate of a CO₂ drop under conditions similar to those expected in deep ocean sequestration [2, 4]. A model was developed assuming that the thickness of the shell is governed by the diffusion of the CO₂ through the hydrate shell and diffusion or convection of dissolved CO₂ away from the hydrate-covered particle. Bounds on the thickness of the initially formed shell, and upon the thicknesses of shells in saturated and unsaturated environments were estimated.

According to the model, a very thin hydrate shell (<0.1 cm) should initially form around drops of CO₂ injected into the deep ocean. If injected into water unsaturated with respect to hydrate forming conditions, a stable hydrate shell thickness on the order of 10⁻² to 10⁻⁴ times the radius of the drop will form. If injected into saturated water, the hydrate will form a thicker shell, possibly approaching 10⁻¹ cm in thickness for growth periods in excess of 100 h. Since the water is saturated with respect to hydrate-forming conditions, the hydrate shell would serve only to slow the diffusion of CO₂ and thus prevent the formation of additional hydrate from the injected CO₂. Saturated conditions could occur in the vicinity of the injection. Under this scenario, additional hydrates could form on the hydrate-covered drop from the CO₂ dissolved in the water. This was the subject of an earlier paper (5).

In the experiments described in the previous section, CO₂ drops were injected into the HVVC and the dissolution of the drops monitored. In the experiment at higher CO₂ concentration, the first drop injected (at 2°C, 145 bar) immediately formed a hydrate shell. In contrast, in the experiment at lower CO₂ concentration, several drops were initially added that did not form a hydrate shell. With each drop the dissolved CO₂ concentration increased. Above 51 mg/g GPS, at conditions near 2°C and 175 bar, subsequent drops formed a hydrate shell within several seconds of injection. The shell was observed to form from a single nucleation point on the drops and rapidly grow to cover the entire drop surface.

Drop dissolution rates, expressed as the rate of radial decrease, as a function of temperature from the

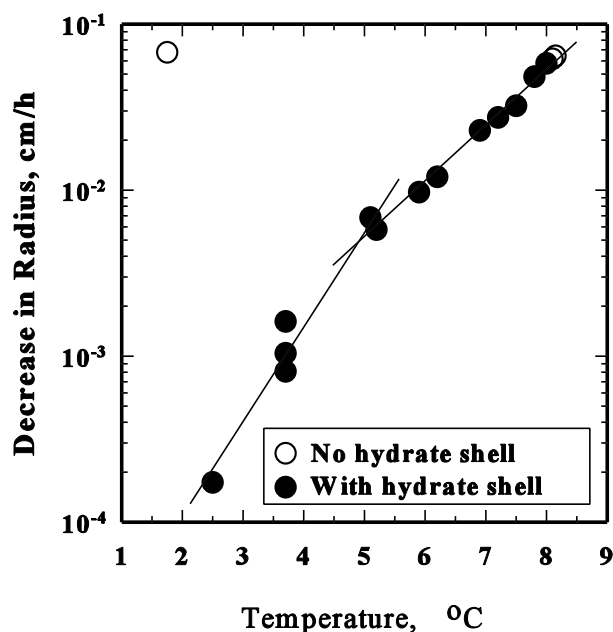


Figure 1. CO₂ drop dissolution in seawater.

experiment at lower CO₂ concentration are shown in Figure 1. The radial measurements were made from video images recorded as the HVVC was warmed from 1.7°C to 8.1°C. A new drop was injected into the HVVC only after complete dissolution of the preceding drop. Formation of the hydrate shell resulted in a decline in the rate of radial decrease of three orders of magnitude when hydrate shells were formed. The rate of shrinkage increased with temperature. This is likely due to thinning of the hydrate shell. This thinning was substantiated by visual observations. The hydrate shell at lower temperature was rough textured; whereas, at higher temperatures the shell was smooth. The different slopes in the data suggest that the shell was not at steady state at the lower temperatures. Additional experiments are planned to determine if this is the case.

Conclusions

Previous experimental results in freshwater and recent results in seawater, along with model predictions, indicate that hydrate shell formation on CO₂ drops would negatively impact attempts to sequester CO₂ in the ocean by direct injection at depths below about 500 m. A thin hydrate shell would stabilize the drop and permit the injected CO₂ to rise to unacceptably shallower depths before dissolution. Hydrate fragments from the drop may also be buoyant owing to trapped CO₂ in the hydrate lattice. Injection strategies that avoid or limit hydrate shell formation will be required for effective sequestration. One strategy would be to design the injection system to insure that the CO₂ concentration in the seawater remains below that required for hydrate formation. Based on the early data from this work, this limit would be near 50 mg CO₂/g seawater at depths currently being considered for direct injection (1000 m to 1500 m). Another strategy would be to dissolve the CO₂ in the seawater prior to encountering depths where hydrate formation would be possible. The gas lift tube dissolution concept of Saito, et al. exemplifies this concept [6]. Direct injection strategies will also be impacted by the effect of turbulence and jet dynamics, areas not covered in the work reported here but which are under investigation by others in projects supported by the Department of Energy through FETC [4].

Future Activities

Current research plans involve renovation of the viewcell facilities used in this work and the construction of a water tunnel facility to better simulate the oceanic environment that would be

experienced by CO₂ injected into the deep ocean. The water tunnel facility is modeled after work previously performed by Maini and Bishnoi [7] and Moo-Young, et al. [8]. The facility will include both low-pressure and high-pressure systems. The low-pressure system will be used to determine critical design parameters necessary to stabilize a bubble or drop in an observation section and to study low-pressure hydrate formers as models of the CO₂/seawater system. The design parameters will be incorporated in the high pressure system that will be used to study the CO₂/seawater system.

Disclaimer

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